

TLI

TYCO LABORATORIES, INC.

BEAR HILL, WALTHAM 54, MASSACHUSETTS

AREA CODE 617

TELEPHONE: 888-1880

AFCRL - 65 - 433

AD 619166

INVESTIGATION OF THE EFFECT OF THE CHEMICAL BOND
ON THE ELECTRONIC PROPERTIES OF
MULTI-COMPONENT SEMICONDUCTORS

by

Arthur J. Rosenberg and Fritz Wald

COPY	OF	RS
HARD COPY	\$. 3.00	
MICROFICHE	\$. 0.75	

Contract No. AF19(628)1615

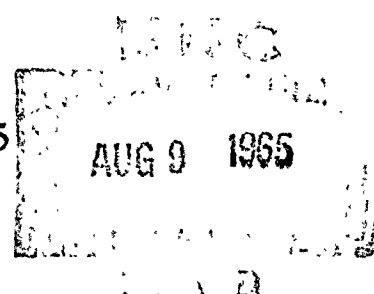
Project No. 5620

Task No. 562001

60P

FINAL REPORT

Covering period June 1, 1962 - May 31, 1965



Prepared for
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

ARCHIVE COPY

Requests for additional copies by agencies of the Department of Defense, their contractors, or other government agencies should be directed to:

DEFENSE DOCUMENTATION CENTER (DDC)

CAMERON STATION

ALEXANDRIA, VIRGINIA 22314

Department of Defense contractors must be established for DDC services or have their "need-to-know" certified by the cognizant military agency of their project or contract.

All other persons and organizations should apply to the:

Clearinghouse for Federal Scientific
and Technical Information (CFSTI)

Sills Building

5285 Port Royal Road

Springfield, Virginia 22151

INVESTIGATION OF THE EFFECT OF THE CHEMICAL BOND
ON THE ELECTRONIC PROPERTIES OF
MULTI-COMPONENT SEMICONDUCTORS

by

Arthur J. Rosenberg and Fritz Wald

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts

Contract No. AF19(628)1615

Project No. 5620

Task No. 562001

FINAL REPORT

Covering period June 1, 1962 -- May 31, 1965

Prepared for

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

CONTENTS

	<u>page no.</u>
I. Abstract	1
II. List of Contributors	1
III. List of Publications with Abstracts	2
A. The Chemical Approach to Semiconductors	2
B. Solid Solutions of CdTe and InTe in PbTe and SnTe	3
C. Constitutional Investigations in the Boron-Platinum System	4
D. Massive Heterovalent Substitutions in Octahedrally Coordinated Semiconductors	4
E. Solid Solutions of CdSe and InSe in PbSe	5
F. Investigations on the Constitution of Certain Binary Boron-Metal Systems	6
IV. Additional Material	6
A. Work on the Silicon-Tellurium System	7
B. Electrical Properties of a Solid Solution Alloy of the PbTe-CdTe System in Comparison with Pure PbTe	7
C. Solid Solubility of PbTe in CdTe	7
D. The GeTe-CdTe System	8
E. A Novel Method of Growing Crystals of Terminal Solid Solutions	9
F. Additional Investigations in the Boron-Platinum System	10
G. Investigations in the Boron-Palladium System	11
H. Travelling Solvent Growth Experiments with Platinum as a Solvent for Boron	13
I. Crystal Growth Experiments with a Gold-Copper Alloy as a Solvent	13
Appendix — Scientific Paper: "Investigations on the Constitution of Certain Binary Boron-Metal Systems"	

I. ABSTRACT

Work on the contract consisted of two distinctly different parts:

A. An investigation of the effects of nonisomorphic alloying on the electronic properties of semiconductors of the IV-VI type with sodium-chloride structures. These experiments were conducted in conjunction with a theoretical concept, the "Chemical Approach to Semiconductors".

B. Experiments directed towards the solution growth of the low temperature modification of boron, the red α -rhombohedral form, which is of interest as a large energy gap elemental semiconductor.

Under (A), detailed investigations on the solid solubilities of CdTe and InTe in PbTe and SnTe, as well as of CdSe and InSe in PbSe were carried out, and pertinent information on the resulting pseudo binary systems was collected. Selected alloys were measured for their electrical properties and the crystallographic and electrical information was used to gain a better understanding about the applicability and limitations of a chemical bond approach to compound semiconductors.

Under (B), the phase diagram of the boron-platinum system was determined and phase information on systems of boron with the elements of groups Ib and IIb and the heavier elements of groups IIIa, IVa, Va, and VIa was collected. Some experiments on the solution growth of the red rhombohedral α -boron modification were carried out.

II. LIST OF CONTRIBUTORS

Dr. Arthur J. Rosenberg, Principal Scientist

Mr. Fritz Wald, Staff Scientist

Dr. Robert Grierson, Staff Scientist

Mr. Richard Stormont, Experimental Assistant

III. LIST OF PUBLICATIONS, WITH ABSTRACTS

A. Physics and Chemistry of Ceramics

Cyrus Klingsberg, Editor
Gordon and Breach, New York, 1963

THE CHEMICAL APPROACH TO SEMICONDUCTORS

Harry C. Gatos

Lincoln Laboratory, Massachusetts Institute of Technology
Department of Metallurgy and Department of Electrical
Engineering, M. I. T.,
Cambridge, Massachusetts
and
Arthur J. Rosenberg
Tyco Laboratories, Inc.

Abstract – The energy band approximation for electron energy levels has been extremely successful in the quantitative treatment of semiconductors. Unfortunately, this treatment entails a complex mathematical formalism that provides little intuitive insight into the design and development of new materials. Such insight is gained, however, through a chemical approach to semiconductors which is based upon two postulates. The first postulate is that the charge carriers (electrons and holes) in intrinsic semiconductors originate in the excitation of bonding electrons to antibonding states. The second postulate is that the charge carriers may be treated as quasi-chemical species within the formalism of chemical thermodynamics and kinetics. These postulates lead to a rational framework for relating the electrical properties of semiconductors to their chemical composition and crystalline structure, and thus provide an effective guide for the design and development of new materials. The salient features of the chemical approach to semiconductor properties are discussed.

SOLID SOLUTIONS OF CdTe AND InTe IN PbTe AND SnTe

I. CRYSTAL CHEMISTRY

Arthur J. Rosenberg, Robert Grierson, J. C. Woolley, and
P. Nikolic

Abstract – Extensive solid solubilities of CdTe (zincblende-type structure) and InTe (B37-type) in each of the rock salt-type compounds, PbTe and SnTe, have been observed. Partial phase diagrams have been determined by thermal analysis and X-ray metallography. The limiting mol fractions, X_m , of the solute in the rock salt-type α phase and the corresponding eutectic temperatures, T_e , are:

$$(\text{PbTe})_{1-x}(\text{CdTe})_x : X_m \sim 0.2, T_e = 866^\circ\text{C};$$

$$(\text{PbTe})_{1-x}(\text{InTe})_x : X_m \sim 0.35, T_e = 646^\circ\text{C};$$

$$(\text{SnTe})_{1-x}(\text{CdTe})_x : X_m \sim 0.11, T_e = 784^\circ\text{C};$$

$$(\text{SnTe})_{1-x}(\text{InTe})_x : X_m \sim 0.53, T_e = 630^\circ\text{C}.$$

The lattice parameters of the α phase decrease linearly with X , even in $(\text{PbTe})_{1-x}(\text{CdTe})_x$, where $a_0(\text{CdTe}) = 6.481 \text{ \AA}$. This is taken as proof that the cadmium atom enters an octahedral interstice of the tellurium atom sublattice; i.e., the formation of the α phase entails the direct replacement of lead by cadmium. The a_0 vs X curve extrapolates to 6.16 \AA at $X = 1$, in agreement with the value predicted for an ionic crystal of CdTe; it is also consistent with the reported lattice parameter of the high-pressure rock-salt form of CdTe, corrected for decompression from 36 kbar. The free energy of formation of the α phase of pure CdTe at room temperature is calculated from the phase diagram to be + 10 kcal per g-atom, in accord with the value calculated from the transformation pressure. The standard enthalpy is + 13 kcal per g-atom, and the standard entropy is + 9 eu. The latter value implies the formation of extra classical particles, such as vacancies, interstitials, or nondegenerate charge carriers, but these alternatives are not consistent with the semiconducting properties and the densities of the α phase.

The extrapolated values of the lattice parameters of $(\text{PbTe})_{1-x}(\text{InTe})_x$ and $(\text{SnTe})_{1-x}(\text{InTe})_x$ give $a_0 = 6.24 \text{ \AA}$ and 6.21 \AA , respectively, for the rock salt-type modification of InTe. The corresponding interatomic separation is intermediate between monovalent and trivalent indium. The qualitative implications of the results are considered from the viewpoints of both valence-band theory and energy-band theory.

C. Trans. Met. Soc., A.I.M.E., 233, 796-799 (1965)

CONSTITUTIONAL INVESTIGATIONS IN THE BORON- PLATINUM SYSTEM

F. Wald and A. J. Rosenberg

Abstract – The general features of the constitution of the B-Pt system were determined using standard metallographic, thermoanalytic, and X-ray diffraction techniques. Three compounds were found. Two of these, Pt_3B and Pt_2B , are formed by peritectic reactions at 825° and 890°C , respectively. The third, Pt_3B_2 , is congruently melting with a flat maximum at 940°C , but decomposes eutectoidally into Pt_2B and boron at $\sim 600^\circ$ to 650°C .

D. J. Phys. Chem. Solids, 1965, Vol. 26, in press

MASSIVE HETEROVALENT SUBSTITUTIONS IN OCTAHEDRALLY COORDINATED SEMICONDUCTORS

Arthur J. Rosenberg and Fritz Wald

Tyco Laboratories, Inc., Waltham, Massachusetts 02154

(Received 13 January 1965)

Abstract – The alloying of indium in Bi_2Se_3 and of cadmium and indium in PbSe and PbTe have been studied using melt-grown crystals containing up to 5 mol percent of the impurity atoms. In each case, the mixed crystal retains the basic crystal structure type of the host crystal, with diminution in the volume of the unit cell. In the lead compounds, the densities of the mixed crystals are in accord with a stoichiometric replacement of cations. The lattice parameter of cadmium-doped PbTe indicates that direct substitution takes place in the octahedral sites of the tellurium atom sublattice,

while, in indium-doped PbTe, the indications are that at least one-third of the impurity atoms enter tetrahedral sites. The magnitude of the Hall coefficient of cadmium-doped PbTe is unchanged from that of PbTe itself. This is taken to mean that two s-like states are split off from the valence bands of the crystal to form a high-lying impurity band. An absence of large changes in the Hall coefficient is also found in cadmium-doped PbSe and indium-doped Bi_2Se_3 , where, again, there is a two-electron deficiency in the valence shell of the impurity atom. By contrast, indium is a donor in the lead compounds. In PbSe, it is a strong donor, still consistent with the separation of two states from the valence band of the host crystal. However, in PbTe it behaves as a weak donor, and suggests, thereby, an ambivalence associated with its distribution between tetrahedral and octahedral sites. The results are discussed in terms of the recent energy band calculations on PbTe by Conklin, Johnson, and Pratt.

E. J. Phys. Chem. Solids, 1965, Vol. 26, in press

SOLID SOLUTIONS OF CdSe AND InSe IN PbSe

Fritz Wald and Arthur J. Rosenberg

Tyco Laboratories, Inc., Waltham, Massachusetts 02154

(Received 13 January 1965)

Abstract — The solid solubilities of CdSe and of InSe in PbSe have been studied by thermal analysis and X-ray metallography. The solubility limit of InSe in PbSe is ~ 4.5 mol percent at the eutectic temperature of 545°C . The solubility limit of CdSe in PbSe is ~ 26 mol percent at 940°C . However, a shift in the apparent eutectic temperature and the appearance of excess selenium in vacuum annealed specimens in this system imply a deviation from ideal pseudo-binary behavior. The cubic rock-salt lattice parameter of specimens with the nominal composition $(\text{PbSe})_{1-x}(\text{CdSe})_x$ over the range of solubility is given by $a_0 = 6.127 - 0.42 X$. By extrapolation to $X = 1$, one obtains $a_0 = 5.71 \text{ \AA}$ for the hypothetical rock-salt modification of CdSe, which is 0.45 \AA less than the similarly derived value

for CdTe. The corresponding differences between the stable tellurides and selenides of barium, strontium, and calcium are 0.41, 0.42, and 0.43 Å, respectively. By contrast, the difference between the lattice parameters of PbTe and PbSe is 0.33 Å. The results are taken to mean that the dissolved cadmium atoms in PbSe and PbTe are largely ionic, in accordance with previous considerations of the electrical properties of the mixed crystals.

F. Accepted for publication in: The Journal of the Less Common Metals, and appended as a scientific paper to this final report:

INVESTIGATIONS ON THE CONSTITUTION OF CERTAIN BINARY BORON-METAL SYSTEMS

by

Fritz Wald and Richard W. Stormont

Tyco Laboratories, Inc., Waltham, Massachusetts 02154

Abstract — Binary systems of boron with copper, silver, gallium, gold, germanium, lead, and tin have been investigated by the usual method of X-ray analysis, optical metallography, and thermal analysis. Except for the boron-copper system, all other investigated systems show large miscibility gaps in the liquid state. The previously reported compounds "CuB₂₂", "AgB₂", and "AuB₂" could not be confirmed. The results are discussed in the light of Samsonov's theory for the formation of borides and Hildebrand's rule about the tendency of binary systems to form miscibility gaps in the liquid state.

IV. ADDITIONAL MATERIAL

In addition to the information gathered completely enough to be published in a final form, a number of tasks were started on both parts of the contract, which led either to negative results, or, after a time, to no relevant results at all. We believe, though, that some of the information is valuable enough to warrant presentation in this report.

A. Work on the Silicon-Tellurium-System

A series of alloys of the general composition $\text{Si}_x\text{Te}_{(1-x)}$, with x between 0.1 and 0.66, have been cast or directionally grown from the melt. The $\text{Si}_{0.1}\text{Te}_{0.9}$ ingot appears to be a single phase solid solution of Si in Te. In all other cases, X-ray diffraction lines corresponding to the intermediate phase SiTe_2 have been observed. The existence of this phase has previously been reported by Weiss and Weiss (Z. Anorg. Chem., 273, 124 (1953), but two other phases reported by them have not been observed. An apparent liquid immiscibility has prevented the casting of macroscopically homogeneous alloys of high silicon content, and silicon diffraction lines were noted for $x = 0.66$. Thermal analysis of the samples containing the SiTe_2 phase revealed two distinct phase changes at approximately 420°C and 660°C . Infrared absorption measurements of SiTe_2 reveal a sharp band edge at 0.6 microns.

B. Electrical Properties of a Solid Solution Alloy of the PbTe-CaTe-System in Comparison with Pure PbTe

<u>Ingot Composition</u>	<u>Density (grams/cc)</u>	<u>Lattice Para-meter (Å)</u>	<u>Seebeck Coeff. (mv/°C)</u>	<u>Resistivity (ohms/cm)</u>	<u>Carrier Conc. (per cc.)</u>	<u>Hall Coeff. (cm³/coul)</u>	<u>Mobility cm²/volt sec.</u>
PbTe	8.253	6.459	+228	3.02×10^{-3}	3.22×10^{18}	1.94	642
Pb _{0.9} Ca _{0.1} Te	7.685	6.457	+249	2.9×10^{-2}	9.17×10^{18}	0.69	23

C. Solid Solubility of PbTe in CdTe

Studies were made to determine the solubility of PbTe in CdTe. Towards this end, a series of alloys containing 2, 4, 6, and 8 mol % PbTe in CdTe were annealed at 900°C for 27 days; and then quenched in water. The lattice spacing of these homogeneous samples was measured, using a diffractometer to determine the exact position of the (531)-reflection at $2\theta \sim 89.3^\circ$. The results are shown in Table 1.

TABLE 1

<u>Composition</u>	<u>2 θ ($^{\circ}$)</u>	<u>a_o (531)</u>
CdTe	89.35 \pm 0.01	6.4812 \pm 0.0006
Cd _{0.98} Pb _{0.02} Te	89.34 \pm 0.01	6.4818 \pm 0.0006
Cd _{0.96} Pb _{0.04} Te	89.33 \pm 0.01	6.4824 \pm 0.0006
Cd _{0.94} Pb _{0.06} Te	89.34 \pm 0.01	6.4818 \pm 0.0006
Cd _{0.92} Pb _{0.08} Te	89.34 \pm 0.01	6.4818 \pm 0.0006

As can be seen, all the measurements are equal, within the small experimental uncertainty. Since there is a tendency towards slightly higher values, compared with CdTe, a small solubility (e.g. < 0.5 mol % PbTe) may result.

D. The GeTe-CdTe System

An investigation into the GeTe-CdTe system was started, to find if any solid solubility of CdTe exists in GeTe.

Metallographic studies were made on a series of alloys containing 1, 3, 5, 10, 15, 20, 30, and 40 mol % CdTe in GeTe, quenched from the melt. A quasi-binary eutectic behavior was found, with CdTe primary crystallization in all alloys containing 10% or more CdTe, and GeTe primary crystallization in all others. From the microphotographs, it was estimated that the pseudo-binary eutectic lies at 8% CdTe (see Figs. 1a - d).

Thermal analysis and X-ray investigations were made on alloys annealed for 15 days at 650°C. The results of the thermal analyses are presented in Fig. 2.

The X-ray investigations were irregular, in that the d-spacing of GeTe changed, even in two-phase alloys. This may be due to our using stoichiometric GeTe (50:50 at. %) instead of the reported non-stoichiometric compositions. GeTe reportedly undergoes some change in lattice parameters between 50.8 and 49.9% Ge. Amounts of Te may also have been lost during the annealing process, which would consequently also lead

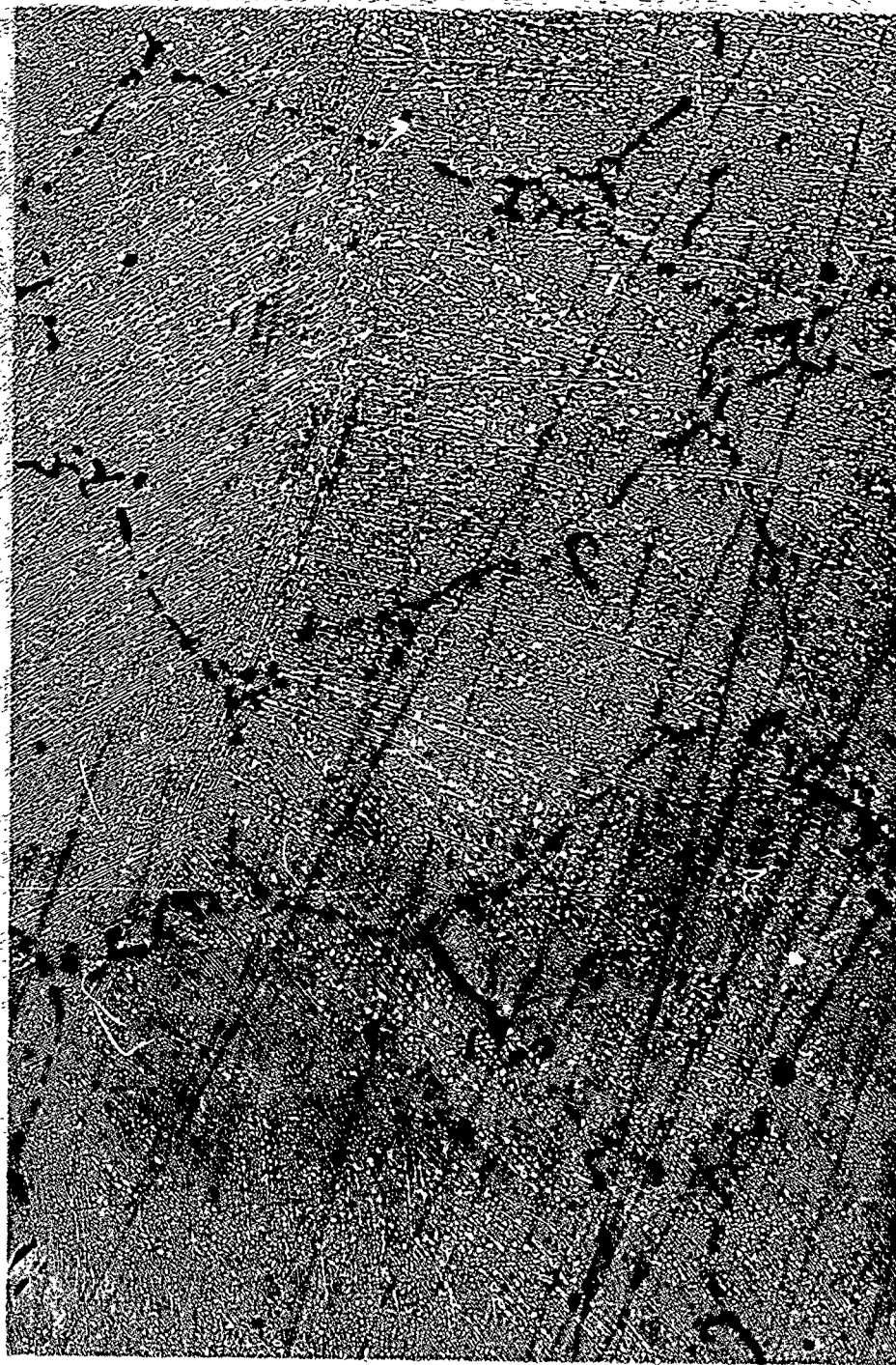


Fig. 1a 99 at % GeTe, 1 at % CdTe, as cast, optical magnification 700x, photographic magnification 1.6x. Etched in dilute aqua regia.

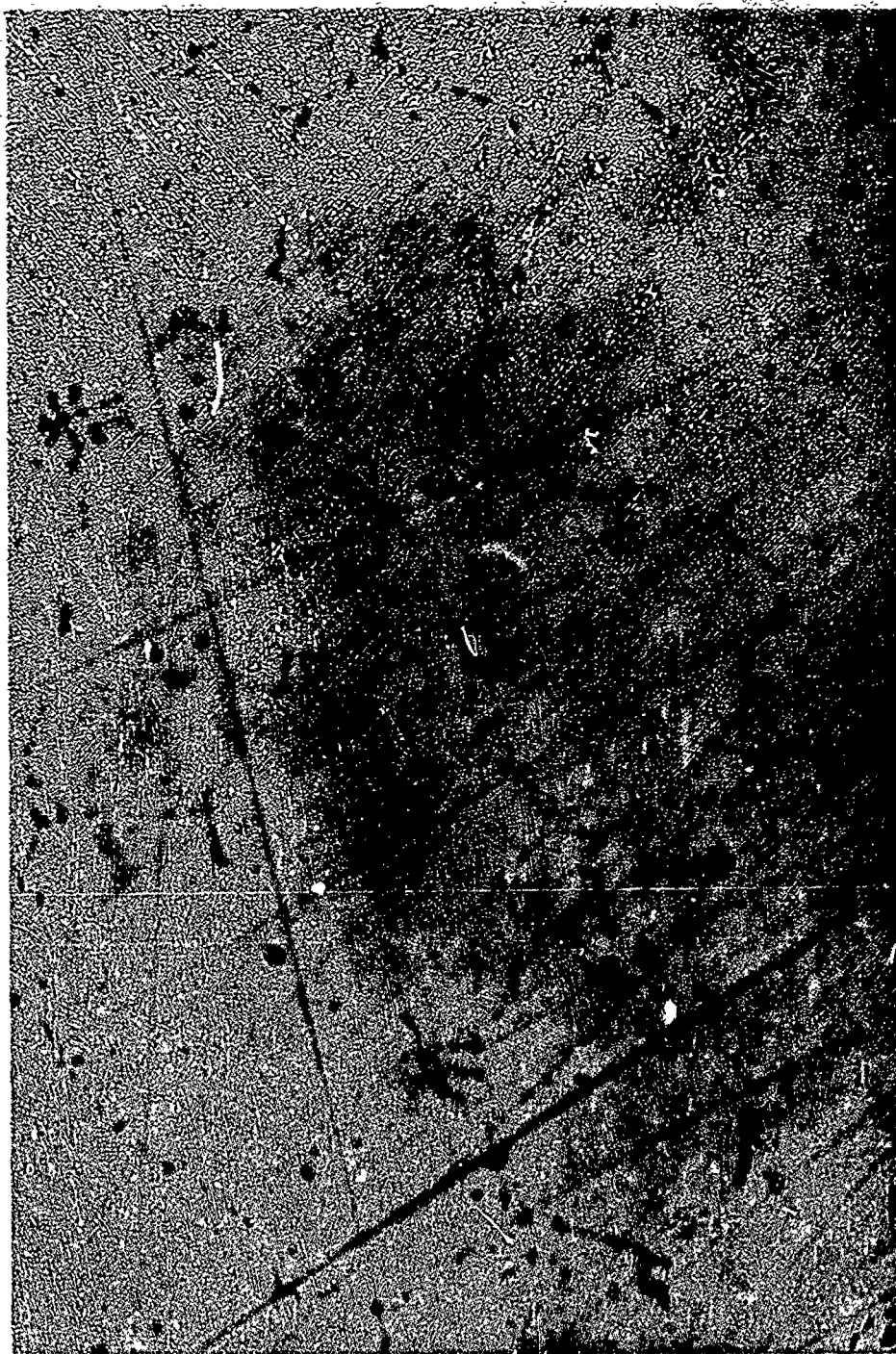


Fig. 1b 95 at % GeTe, 5 at % CdTe, as cast, optical magnification 700x, photographic magnification 1.6x. Etched in dilute aqua regia.



Fig. 1c 90 at % GeTe, 10 at % CdTe, as cast, optical magnification 700x, photographic magnification 1.6x. Etched in dilute aqua regia.



Fig. 1d 60 at % GeTe, 40 at % CdTe, as cast, optical magnification 700x, photographic magnification 1.6x. Etched in dilute aqua regia.

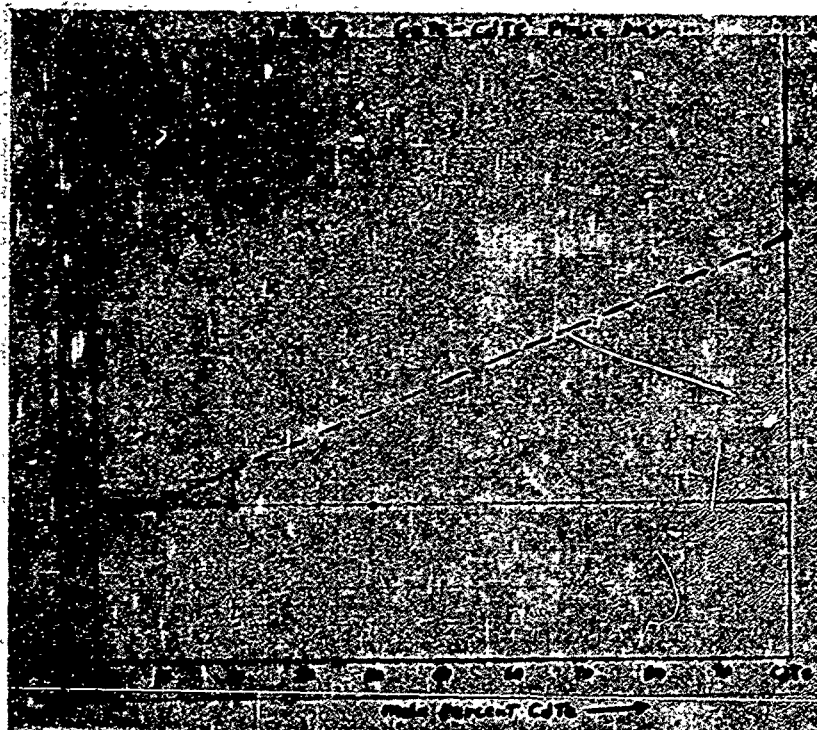


Fig. 2 GeTe-CdTe Phase Diagram

to some changes in the structure. On the other hand, the change in lattice parameter of the constituents of two-phase alloys may be due to non-pseudo-binary behavior of the system. For the purposes of the present investigation though, the system is irrelevant, since no substantial solid solubility was found.

E. A Novel Method of Growing Crystals of Terminal Solid Solutions

A new method of crystal growth for solid solutions is being presented, designed to overcome the disadvantages of the Bridgman growth, which are mainly related to strong segregation and uncertain equilibrium conditions. The new method can also be advantageously used to determine the solidus line by X-ray methods and provide specimens for annealing at lower temperatures. The technique is basically the long-known one of zone melting with a set base temperature. Applied to solid solutions with phase diagrams of the type in Fig. 3, the base temperature specifies, for every composition, how much of the second phase will be dissolved and remain in solid solution.

This information can be used, as mentioned above, for the following purposes:

1. to find the solidus line. An ingot of a composition lying in the $\alpha + \text{liq.}$ region can be zone melted several times to ensure complete equilibrium, which should not be difficult to achieve by this method. The ingot will then be removed, and material taken from its middle. This material can be used for measurements of the lattice parameter, which will denote the solubility at the specific temperature chosen. When these measurements have been carried out for a range of compositions, the saturation solubility can be determined by the break in the curve of lattice parameter vs. composition plot. The method of determination will be similar to that used generally in investigations of this kind, except that the method of equilibrating the alloys will be changed. The results obtained can be checked by thermal analysis.

2. to prepare crystalline ingots. Once the exact solidus line is known, crystalline ingots of specified composition can be prepared by adjusting the base temperature of the zone furnace to the solidus

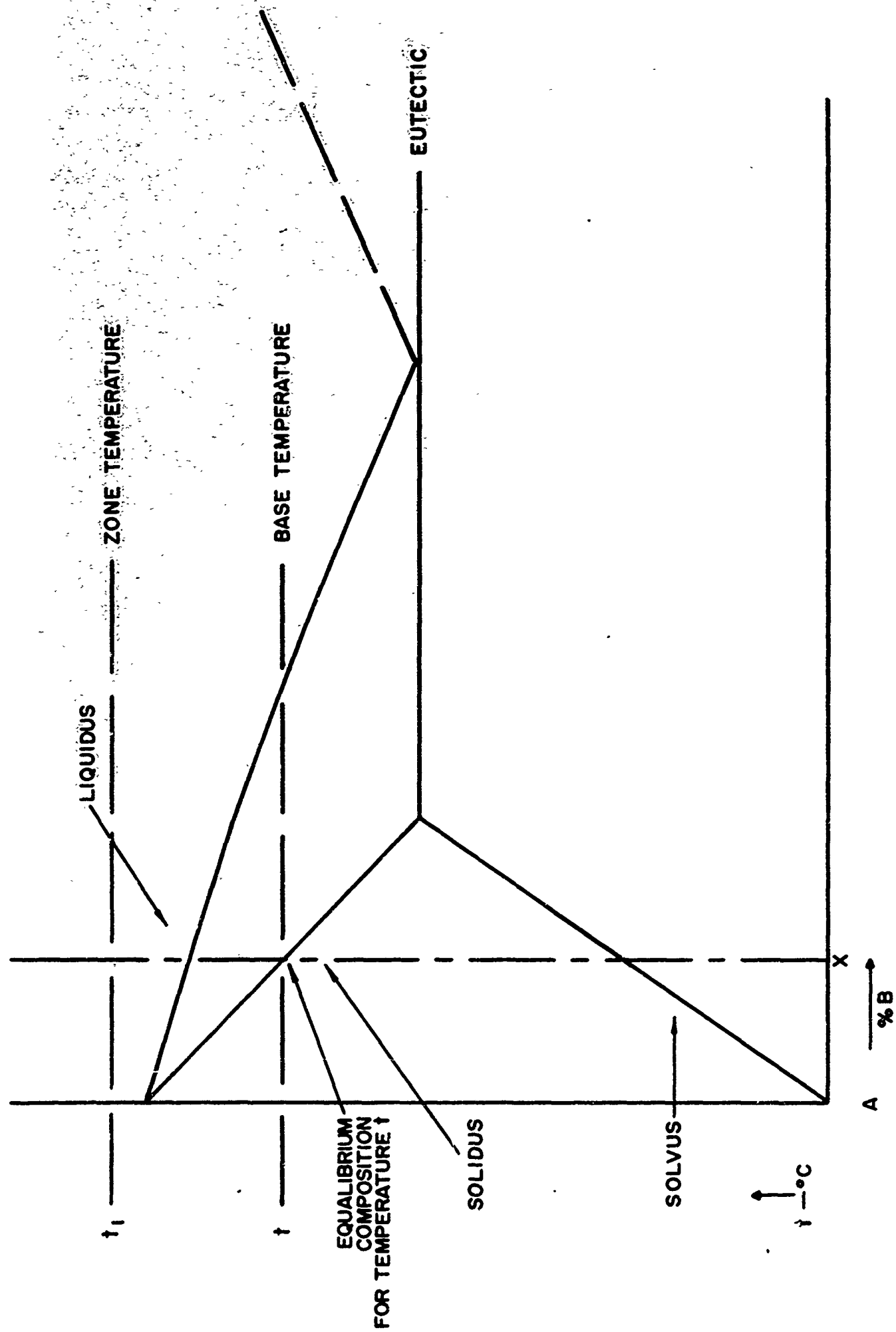


Fig. 3 General case of zoning with set base temperature for a solid solution

temperature of the composition in question and slowly zoning it under conditions optimum for crystal growth. The composition is critically dependent on the accuracy of the base furnace and on the exact determination of the solidus line. Otherwise, either a liquid phase will remain, which could inhibit the growth of large crystals, or the composition will not reach the specified equilibrium.

3. to vary vapor pressure. It will also be possible to vary the vapor pressure of the elements over the melt. An external container can be used which has elemental selenium connected to the zone-ampoule and is regulated at specified temperatures in a furnace. Thus, various elemental pressures can be obtained in the ampoule, which will afford a means of varying the stoichiometry. Samples run under these pressures could then be evaluated by suitable means, i. e. lattice parameter measurements, electrical conductivity, and metallography, to find the solubility limits.

4. to obtain specimens for heat treatment. Specimens can be obtained which can be heat treated at lower temperatures. Then, the solubility below the eutectic limit could be determined by means of lattice parameter measurements. Heat treatments will be shortened, since supersaturated solid solutions easily precipitate. A zoning furnace appropriate for this method has been built, and applied to the PbSe-InSe-system.

F. Additional Investigations in the Boron-Platinum System

1. Solubility of Pt in B

As shown in Fig. 4, the solubility of Pt in B seems to be small, since, of the 1 at % Pt present in the alloy, approximately all is found as a second phase.

2. Sensitivity of Pt_3B for Silicon

Alloys with closely spaced concentrations around the three compounds were annealed for 9 weeks at 750°C in order to determine the



Fig. 4 1 at % B, 99 at % Pt, as cast, optical magnification 100x, photographic magnification 1.6x. Etched in dilute aqua regia, polarized light.

crystal structures and solid solubility ranges. However, alloys around Pt_3B were found to be melted in their quartz tubes after some time. Re-investigation of the peritectic and eutectic temperatures on fresh alloys proved these to be correct. Nevertheless, all alloys with Pt concentrations higher than 66-2/3 at % were wholly or partially melted after annealing at 750°C. An eutectic at ~ 725°C was found in all of them, and the absence of Pt_3B was proven. It was suspected that diffusion from the quartz was responsible for this behavior. It could be shown that the addition of 1 at % Si had a very similar effect. A ~ 2.5 g charge of a fresh alloy with 20 at % boron was analyzed in the thermal analysis apparatus, and repeatedly gave the effect at 825°C ascribed to the peritectic formation of Pt_3B . Addition of ~ 4 mg pure silicon resulted in total disappearance of that effect and the appearance of effects at lower temperatures. It seems that the relative free energies of the liquid and the compound Pt_3B are not too different, so that small additions make the liquid more stable than the compound at lower temperatures. This results in the formation of an eutectic at the same composition, where a compound is formed if no Si is present.

G. Investigations in the Boron-Palladium-System

A literature search revealed evidence strongly contradicting the well-known phase diagram reported by Lehrer⁽¹⁾. Stenberg⁽²⁾ reports the existence of Pd_3B , a composition which coincides with an eutectic reported by Lehrer to exist at ~ 3.5 wt % B. The latter authors also report that a phase which they call Pd_5B_2 (because of its being isomorphous with Mn_5C_2) has the true composition $\text{Pd}_{3.28}\text{B}_2$, therefore being situated rather near the region of Lehrer's Pd_3B_2 and Pd_xB_y , which he (Lehrer) did not closely investigate.

Our own preliminary investigations in the system have resulted in substantial disagreement with Lehrer's diagram in the high Pd-region. We could not detect any sign of melting of alloys with 10, 20, and 25 at % boron in our thermal analysis apparatus, which is capable of reaching temperatures of 1150°C. The three alloys which had been previously reacted by melting the elements together by RF heating not only showed

no sign of any thermal reaction in the apparatus, but were also in perfect physical shape after being heated twice to 1150°C. No signs of melting could be detected. Therefore, we tend to think that Stenberg's⁽²⁾ findings as to the existence of Pd₃B are probably correct, and Lehrer's⁽¹⁾ diagram seems to be wrong, at least in the indicated region. Further investigations are indicated, however.

We were able to gain some thermal data on the system from analysis of three alloys with 33-1/3 at % B ("Pd₂B"), 40 at % B, and 60 at % B (Table 2 presents a summary of the thermal results). These data, however, still do not give any conclusive answer to the constitution of the system at higher boron concentrations. The 33-1/3 at % B alloy, for instance, repeatedly shows four thermal effects. This points to a complex behavior of the system (peritectic or solid state reactions) at this concentration. The rather complex microstructures found in cast alloys of the region tend to confirm this view (Figs. 5a - c). Non-equilibrium structures such as these are generally too complex to interpret with certainty. Annealing experiments in conjunction with X-ray diffraction and metallographic methods will have to be used. The "Widmannstaetten" type structure suggests a solid-state reaction, probably a decomposition of Pd₃B₂ (or Pd_{3.28}B₂) similar to that found in the B-Pt system for Pt₃B₂.

Since Lehrer⁽¹⁾ in the Pd-B system performed his thermal analyses in quartz crucibles, it is possible that the discrepancy between his and Stenberg's⁽²⁾ results can be explained by assuming contamination from the crucibles, similar to our experiences in the Pt-B system. The specific influence of silicon on such boride systems should, therefore, be further investigated.

REFERENCES

1. W. M. Lehrer, Trans. A.I.M.E., 215, 168 - 169 (1959).
2. E. Stenberg, Acta Chem. Scand., 15, 861 - 870 (1961).



Fig. 5a 40 at % B, 60 at % Pd, as cast, optical magnification 140x, photographic magnification 1.6x. Unetched, polarized light.

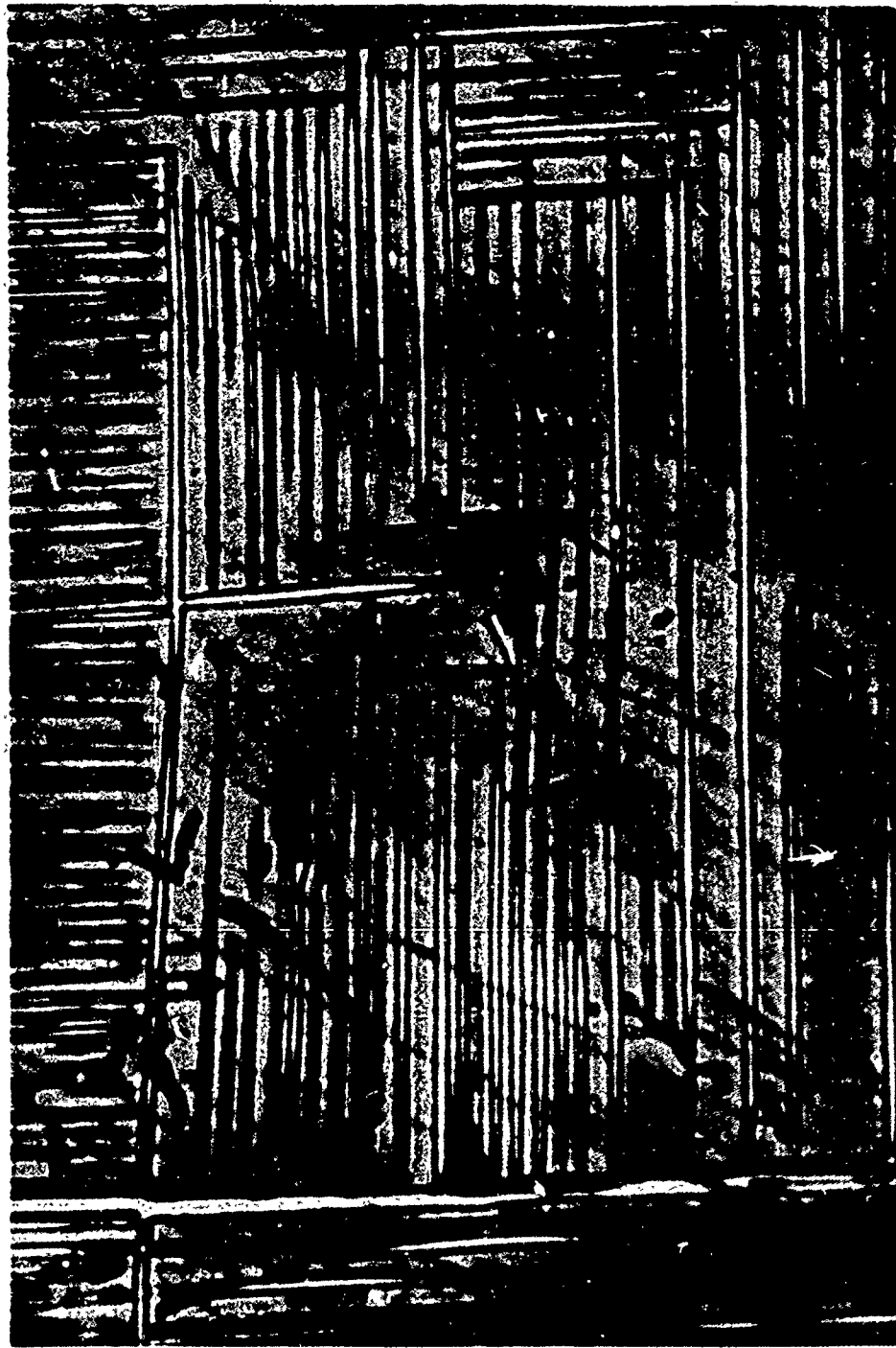


Fig. 5b 40 at % B, 60 at % Pd, as cast, optical magnification 1000x, photographic magnification 1.6x. Unetched, polarized light.



Fig. 5c 33.3 at % B, 66.6 at % Pd, as cast, slowly cooled, optical magnification 140x, photographic magnification 1.6x. Unetched, polarized light.

TABLE 2
Thermal Analysis Results on Boron-Palladium Alloys Below 1150°C

Composition		Thermal Effects (°C)
at % B	at % Pd	
10	90	None below 1150
20	80	None below 1150
24	76	None below 1150
25	75 (Pd ₃ B)	None below 1150
~ 28.6	~ 71.4 (Pd ₅ B ₂)	1057 and 1050
33.3	66.6 (Pd ₂ B)	1007 and 984 and 965 and 953
~ 38	~ 62 (Pd ₃ .28B ₂)	955
40	60 (Pd ₃ B ₂)	954 and 846
50	50 (PdB)	955
60	40 (Pd ₂ B ₃)	963

H. Travelling Solvent Growth Experiments with Platinum as a Solvent for Boron

Table 3 gives a rundown on all experiments which were performed using platinum as a solvent. A detailed discussion for each experiment and the whole complex of difficulties associated with TSM growth using boron as a source and platinum as a solvent is contained in Quarterly Status Report #10. The final conclusions were that platinum is a very inefficient solvent because of the existing compound Pt_3B_2 , which causes the liquidus line on the boron side to be very steep. We also have sufficient reason, from the phase investigations, to doubt that the transformation α - β boron is any higher than $\sim 1050^\circ C$, at least if metals are present. This places a strong limitation on the upper temperature and therefore the temperature gradient which is used in a TSM experiment. As a result, other solvents are needed.

I. Crystal Growth Experiments With a Gold-Copper Alloy as a Solvent

From an extension of the constitutional investigations reported on in the appended scientific paper it appears that the gold-copper alloy with the minimum melting point would be a preferred choice for a solvent.

An alloy containing 20 wt % Cu and 80 wt % Au was therefore prepared and 2 wt % boron was added. Thermal analysis investigations reveal two effects, a strong one at $907^\circ C$ and a weak but clear one at $1061^\circ C$. A microphotograph of this alloy is shown in Fig. 6, revealing that boron is precipitated as primary crystal in a uniform matrix. This leads us to the conclusion that the system contains an eutectic ridge, terminating in the minimum melting point composition of the Au-Cu system.

It can be seen, under polarized light, that the largest part of the boron is the red α -rhombohedral form.

A preliminary solution growth experiment was run for 5 days at a speed of ~ 8 mm/day. Fig. 7 shows clearly that crystal precipitation at the lower end of the ingot has been achieved. The bulk of the precipitated

TABLE 3

Conditions in the First 9 Crystal Growth Experiments by TSM

Run No.	Source material, thickness (mil)	Seed material, thickness (mil)	Solvent material, thickness mil	Top Temp. °C.	Bottom Temp. °C.	Approx. gradient in zone °C/mil	Atmospheric conditions	Means of heating	Running time (hours)
1	float-zoned Boron, 30	float-zoned boron, 50	Pt, 6	~ 930	~ 1000	0.8	vacuum, 1×10^{-3} torr	R. F. graphite susceptor	3
2	float-zoned boron, 60	float-zoned boron, 30	Pt, 6	~ 1075	~ 1050	0.3	vac. 4×10^{-6}	electron beam	5
3	float-zoned boron, 60	float-zoned boron, 30	Pt, 6	~ 1080	~ 1040	0.4	vac. 4×10^{-6}	electron beam	5
4	float-zoned boron, 50	float-zoned boron, 30	Pt, 6	~ 1110	~ 890	2.5	h. p. Ar 500 torr	graphite cloth	5
5	float-zoned boron, 60	—	Pt, 80	~ 1130	~ 930	1.4	flowing h. p. Ar	W-spiral	4
6	float-zoned boron, 100	—	Pt, 80	~ 1130	~ 930	1.1.	vac. 1×10^{-3}	W-spiral	8
7	float-zoned boron, 60	—	Pt, 100	~ 1090	~ 930	1.0	vac. 1×10^{-3}	W-spiral	46
8	float-zoned boron, 50	float-zoned boron, 30	Pt, 3	~ 1080	~ 920	2.0	vac. 1×10^{-3}	W-spiral	~70
9	single-crystal boron, 30	single-crystal boron, 60	Pt, 6	~ 1075	~ 960	1.3	vac. 2.2×10^{-5}	W-spiral	194



Fig. 6 (80 wt % Au, 20 wt % Cu) + 2 wt % B, as cast, optical magnification 140x, photographic magnification 1.6x. Etched in dilute aqua regia, polarized light.



Fig. 7 "THM" run for 5 days ~ 8mm 1 day at 1025°C. Solvent: 80 wt % Au 20 wt % Cu, solute: "Wacker-Boron" (β -rhombohedral), optical magnification 5x, photographic magnification 1.6x. Precipitate: largely red boron.

crystals again proves to be red by inspection with a polarizing microscope. Obviously, the growth speed was too fast, but a properly built crystal growth apparatus could easily rectify this fault. We believe therefore, that following this line of experimentation should lead to the production of reasonably sized red α -boron crystals in a comparatively short time.

APPENDIX

Scientific Paper: "Investigations on the Constitution of
Certain Binary Boron-Metal Systems" by Fritz Wald and
Richard W. Stormont

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

INVESTIGATIONS ON THE CONSTITUTION OF CERTAIN
BINARY BORON-METAL SYSTEMS

by
Fritz Wald and Richard W. Stormont

Scientific Paper
AF 19 (628)-1615

Accepted for publication in: Journal of the Less Common Metals

ABSTRACT

Binary systems of boron with copper, silver, gallium, gold, germanium, lead, and tin have been investigated by the usual methods of X-ray analysis, optical metallography, and thermal analysis.

Except for the boron-copper system all other investigated systems show large miscibility gaps in the liquid state.

The previously reported compounds " CuB_{22} ", " AgB_2 ", and " AuB_2 " could not be confirmed.

The results are discussed in the light of Samsonov's theory for the formation of borides and Hildebrand's rule about the tendency of binary systems to form miscibility gaps in the liquid state.

I. INTRODUCTION

In the course of work on the growth of single crystals of red α -rhombohedral boron from metallic solvents, it seemed advisable to look for metals which do not form borides. This becomes clear if one realizes that the growth rate of the crystal in solution growth methods is, among other factors, strongly dependent on the slope of the liquidus line of the solvent-solute system. Since the growth of isomorphs of boron also limits the upper temperature, and therefore the temperature gradient which can be employed, the slope becomes critically important. [For a general discussion of solution growth methods see ref. 1]. Therefore, in general, boron-metal systems containing borides with a high-boron content are not very efficient solvents for the solution growth of boron crystals.

It was tried, then, to gain constitutional information on boron-metal systems which reportedly, or according to theory, should not form borides. Among these, the systems of boron with Ag, Au, Cu, Ga, Ge, Sn and Pb were chosen for investigation. Prior information on all these systems is rather scarce. Hansen ⁽²⁾ summarizes the older information, according to which boron is not soluble in any of these metals except copper. This system was investigated in some detail by Lihl and Fleischl ⁽³⁾, who reported a eutectic at 2 wt % B, a compound of the approximate composition CuB_{22} , and a small temperature dependent solubility of boron in solid copper (0.06 - 0.09 wt %). K. Mueller and W. Merl ⁽⁴⁾ report on a number of gold systems and find that boron is soluble in liquid gold, but the solid solubility is very small. The melting point of gold is reported increased $> 1100^\circ\text{C}$. Obrowski ⁽⁵⁾ finds a compound " AuB_2 " in this as well as in the silver boron system. Samsonov and co-workers ⁽⁶⁾ investigated the interactions of Ga, In, Tl, Ge, Sn, and Pb with boron, and found no compounds, which they explain in the light of their earlier theory ^(7, 8) concerning the necessity for low first and second ionization potentials of metals to form borides.

II. EXPERIMENTS

Because the metals under investigation have been reported to react with boron only with difficulty, it was felt necessary in all cases to react liquid boron with the liquid metals. Accordingly, an apparatus was built which allowed us, first to melt the boron and, then to cast the molten metal into the crucible with the molten boron, the whole procedure being carried out under an excess pressure of about 1 atm of purified helium. As a crucible material, pressed boron nitride, grade HBR produced by the National Carbon Company, a division of Union Carbide Corporation, was used. This grade was found to be the only commercially available pressed boron nitride suitable to melt boron in. The crucible was heated inductively through a graphite susceptor. It was observed that at temperatures around the melting point of boron the susceptor reacted slowly with the crucible, so that the life of a crucible with a wall thickness of approximately 1/8" was limited to about 5 - 7 melts without fear of carbon contamination.

The minimum purity of the metals used was 99.95%; some of the materials like Ge and Ga were of semiconductor purity. The boron used was obtained either from Johnson Matthey and Mallory Company or from Wacker-Chemie. The minimum purity, according to the manufacturers, was 99.995% B.

Thermal analyses at lower temperatures ($< 1150^{\circ}\text{C}$) were carried out in an evacuable quartz apparatus in boron nitride crucibles, a method described previously ⁽⁹⁾ for boron-platinum alloys. The apparatus was always calibrated against the melting point of the metallic member of the system under investigation. An over-all accuracy of $\pm 4^{\circ}\text{C}$ is reached. High temperature thermal analysis measurements were carried out in only a few instances by a pyrometric method; they are noted as (P) and are subject to a $\pm 30^{\circ}\text{C}$ error.

X-ray investigations were carried out using a Norelco-Diffractometer with CuK_{α} radiation for the determination of the lattice parameters

or, as always in the case of boron, a Debye-Scherrer Camera with 114.59 mm diameter and CoK_α radiation. The patterns were converted into d-spacings using the data of ⁽¹⁰⁾. The obtained boron patterns were then compared with standard patterns of the literature ^(11, 12, 13), and the lattice parameters for the metals were calculated and their changes noted.

Polishing was generally carried out with diamond paste after cutting the little 5 g button melts with a diamond cutting wheel. It should be noted here that polishing proved to be extremely difficult in some cases because of the substantial hardness differences between the phases present. In some cases the surfaces were, therefore, photographed without polishing in an as-cut condition.

III. RESULTS

a) Boron-Silver-System

In this system three alloys were prepared with 10, 66-2/3 (AgB_2), and 75 at % boron. The micrographs are shown in Figs. 1 a-c. It is obvious from these photographs that an almost complete immiscibility in the liquid state is found, because the separation of the two phases seems complete. Fig. 1 b is the alloy with 66-2/3 at % boron, which had been annealed for one month at 900°C. No diffusion between the two interfaces could be observed. Fig. 2 shows that some boron is, nevertheless, dissolved to form a degenerate eutectic. The melting point of silver is unchanged in all alloys within the limits of accuracy of our equipment. It can be observed, too, that the boron which is part of the eutectic structure appears in the characteristic color of the red α -boron form if viewed under polarized light. We therefore conclude that the compound " AgB_2 " does not exist. The system is an almost completely monotectic one, primary boron crystals could only be observed in very small numbers. The X-ray results confirm this point of view, since no lines corresponding to a hexagonal " AgB_2 " are found. The lattice parameter of silver and the d-spacings of β -boron are unchanged from the literature values. Some very weak lines

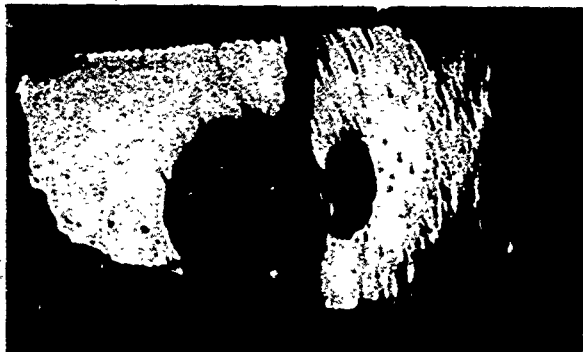


Fig. 1a 10 at % B, 90 at % Ag, as cast, optical magnification 5x. Unetched.



Fig. 1b 66.6 at % B, 33.3 at % Ag, 1 month 900°C, optical magnification 5x. Unetched

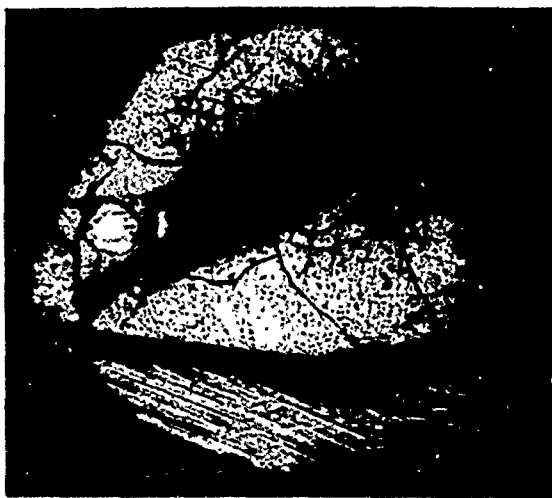


Fig. 1c 75 at % B, 25 at % Ag, as cast, optical magnification 5x. Unetched.



Fig. 2 66.6 at % B, 33.3 at % Ag, as cast, optical magnification 1000x. Unetched, polarized light.

not attributable to either β -boron, silver, or " AgB_2 " are found to be present. Some of these lines can be assigned to other forms of boron, but others always remain mysterious. This seems to confirm, in general, the findings of other investigators on boron, who often suspected that more metastable or even stable isomorphs of boron might exist.

b) Boron-Gold-System

In this system 8 alloys were prepared, containing 5, 10, 20, 50, 60, $66\frac{2}{3}$ (AuB_2), 75, and 80 at % boron.

Thermal measurements on the melting point of gold showed that it decreased to $1056 \pm 3^\circ\text{C}$. The results on all alloys are presented in Table I. Photomicrographs reveal that the eutectic lies at gold concentrations higher than 95 at % (Fig. 3). In Figs. 4 a and b, an alloy with 20 at % B is shown, still possessing a regular distribution of boron primary crystals in a matrix of practically pure gold. It is clearly observed that part of these primary crystals are red under polarized light, proving that the $\beta \rightarrow \alpha$ boron transformation does not lie too much above the eutectic, since the bulk of the primary crystals already in this alloy is β -boron. Fig. 5 a and b show that, at 50 and 75 at % B, the distribution of the boron has become irregular; large islands of boron which have no definite crystalline shape are observed. We, therefore, believe, that at these concentrations a miscibility gap in the liquid state exists. Annealing of the alloy with $66\frac{2}{3}$ at % Au for 2 months at 1000°C did not change its microstructure. The determination of the lattice parameter of gold leads to a value of $4.080 \pm 0.005 \text{ \AA}$. It could indicate a very small solubility of boron in gold, but the accuracy of the determination is not high enough to decide this definitely.

In order to decide approximately what the concentration distribution between α and β -boron in the alloys was, the gold matrix of alloys with 5, 10, and 20 at % boron was dissolved in mercury. The undissolved boron could easily be separated from the amalgam by floatation with isopropyl alcohol, which was subsequently evaporated. The residue gained by this

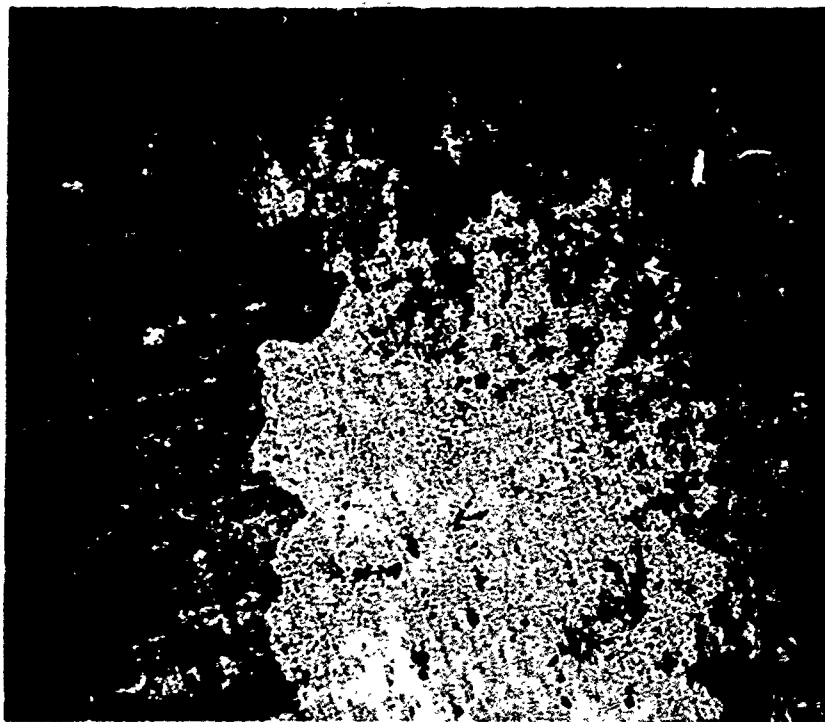


Fig. 3 5 at % B, 95 at % Au, as cast, optical magnification 70x. Etched in dilute aqua regia, polarized light.



Fig. 4a 20 at % B, 80 at % Au, as cast, optical magnification 70x. Etched in dilute aqua regia, polarized light.

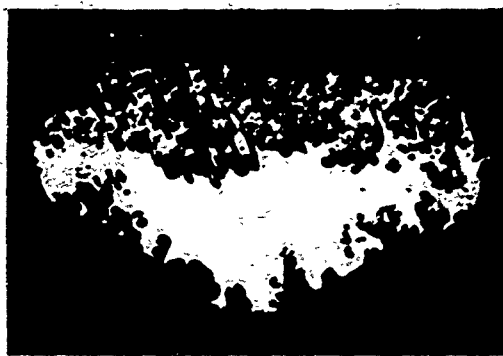


Fig. 4b 20 at % B, 80 at % Au, as cast, optical magnification 5x. Unetched.



Fig. 5a 50 at% B, 50 at % Au, as cast, optical magnification 5x. Unetched.

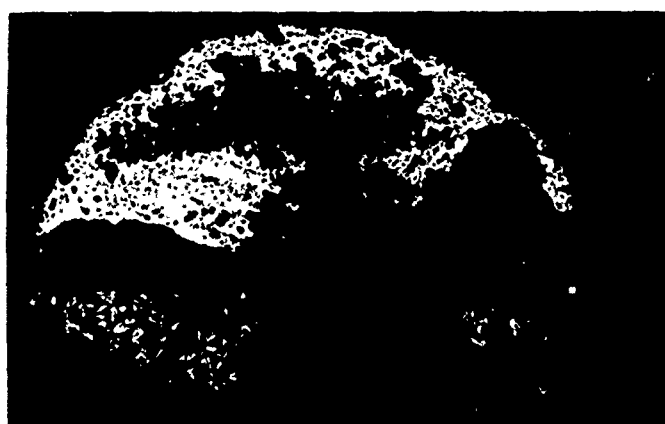


Fig. 5b 75 at % B, 25 at % Au, as cast, optical magnification 5x. Unetched.

TABLE I

Thermal Analysis Results for the Eutectic in Gold-Boron-Alloys

Composition		Eutectic Temperature ° C
<u>at % Au</u>	<u>at % B</u>	
95	5	1056
90	10	1058
80	20	1057
50	50	1056
40	60	1056
33-1/3	66-2/3	1057
25	75	1053
20	80	1055

method was first inspected under a microscope to determine whether red α -rhombohedral boron could be found, and then filled in a glass capillary for X-ray analysis. The expected results did not materialize. Lines of the β -rhombohedral form of boron were always very prominent and easily measured, but a definite spectrum containing all the reported red-boron lines could not be detected in any of the powders, despite the fact that red boron crystals appeared in the microphotographs. A typical pattern is given in Table II. It seems, that in all alloys the α -boron concentration was very small; no estimate of the relative distribution between α and β -boron could therefore be made. The results of these patterns prove, though, that the solid solubility of gold in boron is very small, if not entirely absent. No lines of the reported " AuB_2 " could be detected in any of the X-ray analyses of specimens, complete, and dissolved in mercury. Therefore, we conclude from our combined results that this compound does not exist.

c) Boron-Copper-System

Seven alloys with 1, 5, 10, 25, 50, 75, and 90 at % boron were prepared for the investigation. Thermal analysis results are presented in Table III.

The general outlay of the system as presented by Lihl and Fleischl⁽³⁾ seems valid but has to be considerably modified. The eutectic temperature is found to be 1009°C and the eutectic composition seems to be shifted to higher boron contents than 2 wt % (10 at %) B as seen in Fig. 6 (photomicrograph of an alloy with 10 at % B). A large amount of copper primary crystals are visible in the eutectic matrix. Fig. 7 gives a picture of an alloy with 25 at % B showing just a few boron primary crystals, and Fig. 8 pictures an alloy with 50 at % B showing large amounts of primary crystals. The third thermal effect in the alloys on the boron side of the eutectic cannot, as yet, be explained. From the photomicrographs of an alloy with 90 at % B as cast and annealed for 21 days at 1000°C (Fig. 9) and from the X-ray results on these same alloys it is concluded that the compound " CuB_{22} " does not exist. This is also amplified by the fact that red α -boron forms part of

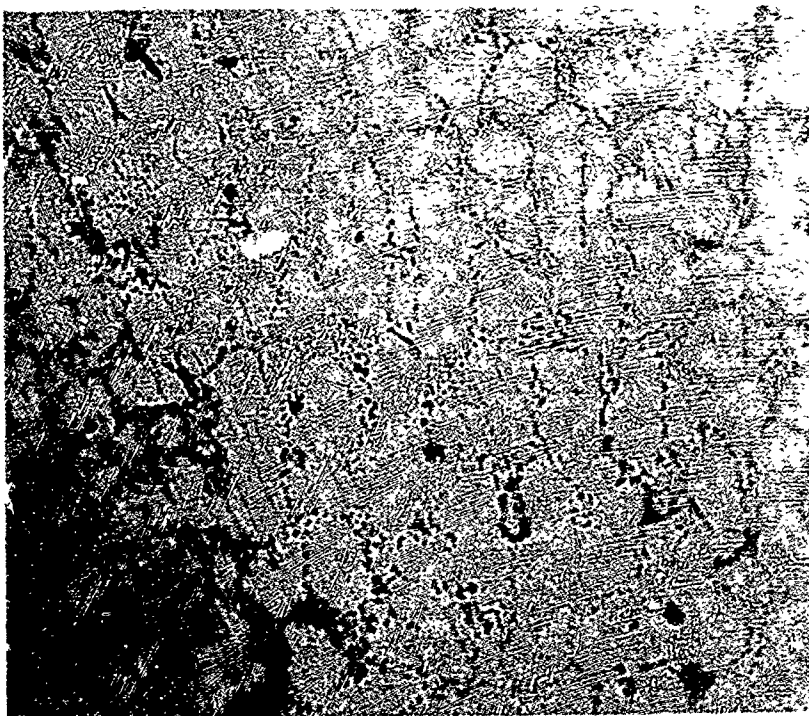


Fig. 6 10 at % B, 90 at % Cu, as cast, optical magnification 300x. Unetched, polarized light.

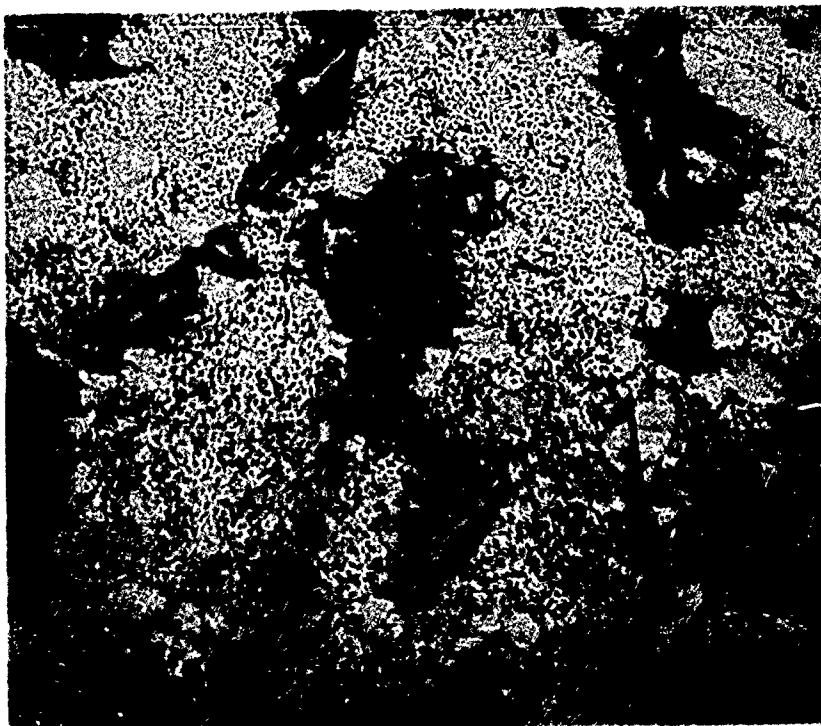


Fig. 7 25 at % B, 75 at % Cu, as cast, optical magnification 300x. Unetched, polarized light.

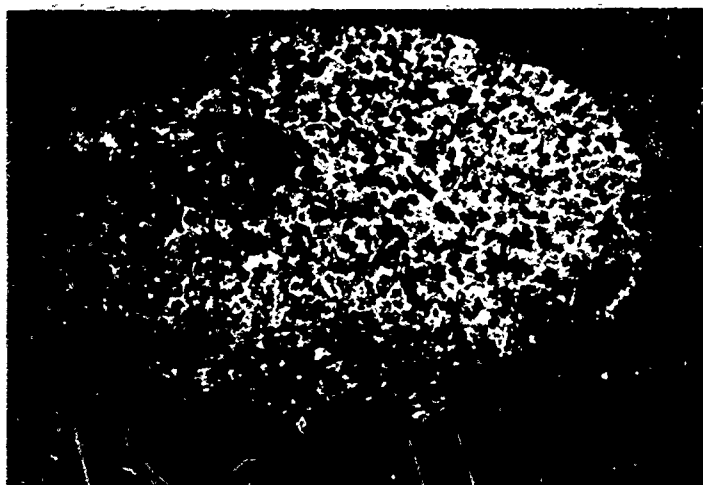


Fig. 8 50 at % B, 50 at % Cu, as cast, optical magnification 5x. Unetched, polarized light.



Fig. 9 90 at % L, 10 at % Cu, 21 days 1000°C, optical magnification 100x. Unetched, polarized light.

TABLE II

Original Alloy Composition: 95 at % Au
5 at % B

(Gold extracted with mercury; residue boron X-rayed.)

Co k_{α} - radiation (Fe-Filter)

Exposure for 16 hrs. at 49 kV, 8 mA

Line	d-spacing (\AA)	Intensity	Assigned to*	Line	d-spacing (\AA)	Intensity	Assigned to*
1	8.00	m	β	25	2.517	w	β
2	7.45	mw	β	26	2.469	m	β
3	5.48	w	β	27	2.403	ms	β
4	5.05	vs	β	28	2.358	s	β
5	4.93	mw	?	29	2.328	vw	β
6	4.65	s	β	30	2.236	ms	β t?
7	4.50	w	β	31	2.192	w	β
8	4.405	w	β	32	2.162	w	α ?
9	4.23	w	β	33	2.111	w	α ?
10	4.13	mw	α ?	34	2.068	vw	β
11	3.98	m	β	35	2.042	ms	β
12	3.88	vvw	β t?	36	1.985	vvw	?
13	3.69	m	β	37	1.960	mw	?
14	3.53	m	β	38	1.912	vvw	?
15	3.415	w	β	39	1.811	s	β
16	3.33	s	β t?	40	1.759	m	β
17	3.24	vvw	β	41	1.735	vvw	?
18	3.165	ms	β t?	42	1.705	w	β
19	3.045	vvw	β	43	1.674	vw	β
20	2.97	s	β	44	1.648	vw	β
21	2.91	vvw	β t?	45	1.627	w	?
22	2.83	s	β	46	1.605	w	β
23	2.75	s	β	47	1.583	vvw	β
24	2.59	vw	β	48	1.546	ms	β

TABLE II (cont.)

<u>Line</u>	<u>d-spacing (\AA)</u>	<u>Intensity</u>	<u>Assigned to*</u>
49	1.494	m	?
50	1.481	vvw	β
51	1.443	s	β
52	1.429	ms	β
53	1.416	m	β

* β = β Rhombohedral

α = α Rhombohedral

β_t = β Tetragonal

TABLE III

Thermal Analysis Results on Copper-Boron Alloys

Composition		Thermal Arrests Found		
at % Cu	at % B	at °C		
99	1	1074	1005	
95	5	1052	1007	(1000?)
90	10	1038	1008	(1000?)
75	25	1018	1009	
50	50	1460(P)*	1022	1008
25	75	1780(P)	1022	1008
90	10	1955(P)	1024	1008
0	100	2045(P)		

*P = Pyrometric Measurement

the eutectic. The X-ray results on this particular alloy are nevertheless extremely interesting. In this alloy we observed a strong spectrum of lines, belonging to the β -tetragonal form, together with β -rhombohedral and α -rhombohedral boron. Indexing of the β -tetragonal spectrum revealed that the a-axis was changed to $a = 11.26 \text{ \AA}$, whereas the c-axis seemed unchanged from 14.14 \AA . These values, however, have to be regarded as preliminary, since the accuracy of the determination was not high. Indexing of the copper lines revealed $a_0 = 3.614 \pm 0.002 \text{ \AA}$ changed only very little from pure copper, the solubility therefore is believed small. The conclusion regarding the thermal effect found at 1022°C would then be to suggest that the observed effect represents a transformation of boron, probably associated with a change in solubility for copper, which would explain the strong thermal effect. If this hypothesis could be proven it would be the first time, that any transformation of boron was reproducibly measured, even if it is changed by a solubility for copper. Further work in this system is needed in order to clarify our preliminary experiments and somewhat speculative views in this direction.

d) Boron-Gallium-System

Two alloys containing 25 and 50 at % B were prepared in this system. Only X-ray methods were used to examine the boron. The d-spacings of the β -rhombohedral boron are unchanged. No indications for compound formation were detected contrary to the observations of Chretien and Laveant⁽¹⁴⁾, however as in all other investigated cases, a few lines were found which could not be assigned to any boron modification.

e) Boron-Germanium-System

Two alloys were made in this system containing 25 and 50 at % boron. As can be seen from Figs. 10a and b this system, too, contains a large liquid immiscibility region. X-ray results in accordance with Samsonov⁽⁶⁾ did not show any solubility for boron in germanium, the lattice parameter of germanium was found as $5.6574 \pm 0.0005 \text{ \AA}$. Also, the



Fig. 10a 25 at B, 75 at % Ge, as cast, optical magnification 5x. Unetched, polarized light.



Fig. 10b 50 at % B, 50 at % Ge, 1 month 900°C, optical magnification 5x. Unetched, polarized light.

d-spacings of β -boron were unchanged. The mp of germanium was determined to 931°C. It can be seen in Fig. 10, that an appreciable amount of boron primary crystals is found in the germanium. It is obvious that the miscibility gap does not extend all the way to 100% germanium.

f) Boron-Lead-System

One alloy was prepared here containing 25 at % B. Due to the low boiling point of lead, considerable losses were encountered; also heavy stirring of the melt took place. Fig. 11, shows that boron and lead are immiscible in the liquid state to a large extent, since boron droplets can be found, frozen in the lead matrix. The melting point of lead was found unchanged. X-ray investigations were not conducted in this system.

g) Boron-Tin-System

Only an alloy with 25 at % tin was prepared. From Fig. 11 it becomes obvious that an almost total liquid immiscibility is found. The melting point of tin is unchanged, and no primary crystals of boron were found in tin. X-ray results indicated no solid solubility of either partner in the other.

IV. DISCUSSION

It has been pointed out by Post ⁽¹⁵⁾ that one of the shortcomings of Samsonov's ^(6, 7, 8) theory on the formation of borides is that it cannot explain the existence of the diborides of gold and silver, since both of these metals exceed, by a large margin, the limiting values of the first and second ionization potentials given by the Russian workers. The same argument could also have been applied to the existence of the reported copper boride "CuB₂₂". From the results presented in this paper it is clear that these three compounds do not exist, a fact which should then tend to support the postulates of Samsonov regarding the importance of the first and

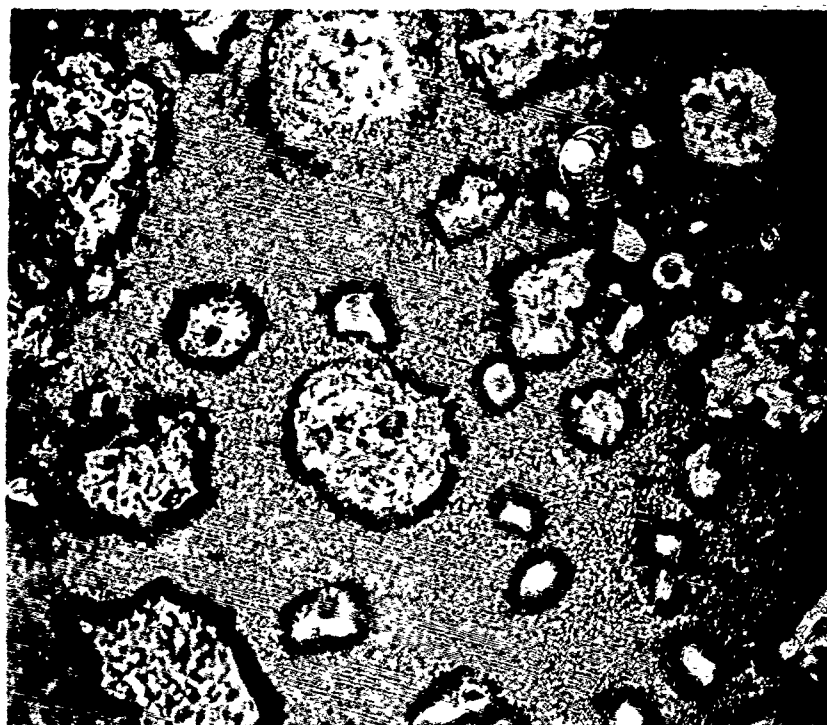


Fig. 11 25 at % B, 75 at % Pb (nominal), as cast, optical magnification 350x. Unetched polarized light.



Fig. 12 25 at % B, 75 at % Sn, as cast, optical magnification 5x. Unetched.

second ionization energy to boride formation. We feel, therefore, justified to assume that his conclusions can be extended to the metals Zn, Cd, and Hg, which have never been investigated, as well as to antimony, the only other element which was never investigated for its reactions towards boron.

The proven absence of any compounds greatly facilitates the application of Hildebrand's Rule ⁽¹⁶⁾ to systems of metals with boron in order to try to detect any tendency towards the formation of systems with liquid miscibility gaps. This rule is based on internal pressure considerations; the solution parameters δ of the equation

$$\frac{V_1 + V_2}{2} (\delta_1 - \delta_2)^2 < 2RT \quad (16 \text{ p. 333})$$

have been calculated for almost all elements (16 p. 323 - 324) (V is the atomic volume.) This rule has also been refined recently by Mott ⁽¹⁷⁾.

Application of this rule to the boron-metal systems discussed in this paper gives total qualitative agreement with experiment, inasmuch as the rule requires that, except for copper, all other systems of boron with the investigated metals should form miscibility gaps. The result was independent, no matter which rule was used, Hildebrand's original one, or the modified one according to Mott. It was, however, not possible to draw any quantitative conclusions about the extent of the miscibility gap from the comparison of deviations of the numerical values of the systems from 2 RT. Extension of the rule to the systems of boron with Zn, Cd, Hg, In, Tl, Sb, and Bi, which could not be investigated because of the high vapor pressures of the elements, revealed that all these elements should form monotectic systems with boron. It seems, therefore, that the boron-copper system holds a unique position in all binary boron systems, being the only simple eutectic system containing neither a compound nor a monotectic reaction.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Badri Das and Dr. Gunther Wolff of this laboratory for valuable discussions and the United States Air Force, Cambridge Research Laboratories for support under Contract AF 19 (628)-1615.

REFERENCES

1. G. A. Wolff and A. I. Mlavsky, Proceedings of the International Conference on Adsorption and Crystal Growth, Nancy, France, June 1965.
2. M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw Hill, 1958.
3. F. Lihl and O. Fleishl, Metall, 8, #1/2, pp. 11 - 19 (1954).
4. K. Mueller and W. Merl, Elekrotechnische Zeitschrift, 80, #15, pp. 515 - 518 (1959).
5. W. Obrowski, Naturwissenschaften, 48, 428 (1961).
6. G. V. Samsonov, N. N. Zhuravlev, Yu. B. Paderno, O. I. Shulishova, and T. I. Serebryakova, Zhurnal strukt. Khimii, U.S.S.R., #4, pp. 458 - 463 (1960).
7. V. S. Neshpor and G. V. Samsonov, Russ. Journal Inorg. Chemistry, 4, 893 - 896 (1959).
8. G. V. Samsonov and V. S. Neshpor, Dokl. Akad. Nauk., U.S.S.R., Ser. Fiz., 3, 1029 - 1031 (1959).
9. F. Wald and A. J. Rosenberg, Trans. Met. Soc. A.I.M.E., 233, 796 - 799 (1965).
10. W. Parrish, M. G. Ekstein, and B. W. Irwin, Data for X-ray Analysis, Philips Technical Library 1953.
11. A. E. Newkirk in Borax to Boranes, American Chemical Society, 1961.
12. F. H. Horn, Journal Appl. Physics, 30, 1612 - 1613 (1959).
13. B. F. Decker and J. S. Kasper, Acta Cryst., 12, 503 - 506 (1959).
14. A. Chretien and P. Laveant, Compt. Rend., 252, 134 - 135 (1961).
15. B. Post in Boron, Metallo Boron Compounds and Boranes, Interscience Publishers, 1964.